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THE SECONDARY ENRICHMENT OF SILVER ORES

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INTRODUCTION

The past half-century has been a period of rapid development of mines and mining, both in America and in other countries, and as a consequence, the basal facts regarding the occurrence of ores are now comparatively well understood. The geologic causes for the location of ore-bodies in certain zones or horizons are in many cases known, and many former theories are generally accepted as facts. The transportation of ores by aqueous solutions, the origin of some of these solutions in cooling igneous magmas, and the secondary enrichment of many ore-bodies through the agency of meteoric waters; such are some of the ideas which have withstood prolonged criticism and have become established tenets of geologic faith. But beyond basal facts, adduced almost solely from field evidence, our knowledge of the mechanism of ore depositions is somewhat vague and unsatisfactory. Only prolonged investigation along chemical and physico-chemical lines will render possible a reasonably accurate understanding of the complex composition of ore-bearing solutions, of the reactions of these solutions with the wall rocks, of the causes for the deposition of minerals from them, and of many other problems connected with the deposition of ores.

At the present time the problems most important and most amenable to solution are those of secondary enrichment; most important, because many of the most valuable deposits were concentrated in this way; most amenable to treatment, because many of the factors of the problems are known, i.e., temperature, pressure, concentrations of solutions, and the chemical nature of the reacting solutions and of the minerals affected.

The principles of secondary enrichment have been outlined by Penrose,[1] S. F. Emmons,[2] Weed,[3] Van Hise,[4] Lindgren,[5] and others, and confirmed by the work of many investigators. In a few cases the chemical reactions which take place have been studied in some detail. Brokaw[6] and McCaughey[7] have investigated the solution of gold in surface waters; Van Hise,[8] Leith, and their associates at the University of Wisconsin have studied the deposition and enrichment of the Lake Superior iron ores; Gottschalk and Buehler[9] have shown the reactions by which the sulphides of iron, lead, zinc, and other metals are taken into solution; and Allen[10] has precipitated pyrite and marcasite under natural conditions.

The processes of the secondary enrichment of silver are of much interest both because they are of widespread occurrence and because a relatively small amount of secondary enrichment may render a low-grade deposit commercially profitable. There is a great variety of secondary silver minerals, and some of them may be deposited even at considerable depths. The mechanism of this downward migration has been discussed by many writers. Near the surface, some have supposed, the silver was dissolved by sulphate solutions, others have regarded chloride waters as increasing the solubility, and still others have assumed the agency of carbonate waters. At greater depths, the precipitation has been thought to be due to the action of hydrogen sulphide or of other sulphides, to the reduction of sulphate solutions by organic matter, or to other causes. The work described in this paper was undertaken to test some of the hypotheses mentioned and to discover if possible in the laboratory the actual extent and speed of the reactions that were found to take place. While much remains to be done, the results herein presented are such as to indicate with some degree of certainty the probable reactions which take place in the solution of silver ores by meteoric waters, and, to a less extent, those which occur in their precipitation.

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[1] Penrose, "Superficial Alteration of Ore Deposits," *Jour. Geol.*, II (1904), 288.

[2] S. F. Emmons, "The Secondary Enrichment of Ore Deposits," *Trans. A.I.M.E.*, XXX (1900), 177.

[3] Weed, "The Enrichment of Gold and Silver Veins," *ibid.*, p. 424.

[4] Van Hise, "Some Principles Controlling the Deposition of Ores," *ibid.*, p. 27.

[5] Lindgren, "Copper Deposits of the Clifton Morenci District," *U.S.G.S.*, XLIII (1905), 177.

[6] Brokaw, *Journal of Geology*, XVIII (1910), 321.

[7] McCaughey, *Jour. Am. Chem. Soc.*, XXXI (1909), 1263.

[8] Van Hise and Leith, *U.S.G.S. Monograph* 52 (1911).

[9] Gottschalk and Buehler, *Economic Geology*, VII (1912), 15.

[10] Allen, *Am. Jour. Sci.* (4), XXXIII (1912), 169.

DEFINITION OF TERMS

The terms "primary" and "secondary" have not always been employed with precise meaning and their use is likely to be attended with some confusion. Wherever introduced into this paper, they are used in a genetic sense. Unless otherwise indicated, the term "primary" implies the agency of hot ascending waters; "secondary," that of cold meteoric waters. It is commonly recognized that some silver ores have been deposited by the agency of cold sulphate solutions in rocks devoid of sulphides.[1] Such deposits might be termed primary, but in their chemical aspects they are secondary, since they differ from those which ordinarily would be termed secondary only in the distance the silver solutions have been carried and in that they have been deposited outside of some zone of primary minerals. As regards their origin through the solution of some truly primary silver mineral, their method of transportation in solution, and the methods of their precipitation, they do not differ from ores precipitated in a silver lode after having been transported a short distance.

SCOPE OF THE DISCUSSION

A study of the literature of silver deposits brings out the fact that all of the silver minerals except the chloride may have either a primary or a secondary origin. These minerals include, in addi tion to compounds of silver with a single acid element, many double compounds, particularly with arsenic, antimony, and tellurium. Argentiferous galena and tetrahedrite are likewise very common sources of silver. Since a description of the secondary enrichment of any metal must account fully for the processes of its solution in meteoric waters, its transportation by, and its precipitation from, them, a complete study of the processes of the secondary enrichment of silver must involve also an explanation of the migration of the sulphides of lead, copper, arsenic, and antimony, in the same ground-waters that carry silver.

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[1] W. H. Emmons, "The Cashin Mine, Montrose Co., Colo.," *U.S.G.S. Bull.* 285 (1905), 125.

PREVIOUS WORK—EXPERIMENTAL

Experimental data bearing on this problem are few, since those who have touched the question in the laboratory have rarely worked under the conditions which commonly obtain in secondarily enriched ore deposits; i.e., low temperatures, small concentrations, low pressures, and a somewhat narrow range of possibilities in the way of chemical composition. Johnston[1] showed that silver carbonate will dissolve in water saturated with carbon dioxide at 15° C. to the extent of 0.846 gm. per liter. Senarmont[2] and Rickard[3] have demonstrated that native silver may be precipitated from silver solutions by organic or carbonaceous matter. Van Hise[4] states that silver sulphide is soluble in solutions of alkaline carbonates, but the writer has been unable to find reference to any experimental confirmation of this statement.

A few experiments have also been made under conditions within the range of possibility as to composition, though not as to temperature and pressure. Spring[5] showed that at pressures of 6,500 atmospheres silver sulphide was formed from its elements. Moesta[6] obtained metallic silver by passing steam at 100 C. over silver sulphide, and Plattner[1] obtained it by passing oxygen at 100° C.–120° C. over the same substance. Stokes[2] found that the reactions $Fe_2(SO_4)_3+2Ag=Ag_2SO_4+2FeSO_4$ and $2CuSO_4+2Ag=Cu_2SO_4+Ag_2SO_4$ were reversible; silver was dissolved on heating, and reprecipitated on cooling.

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[1] G. S. Johnston, *Chem. N.*, LIV (1886), 75.

[2] Senarmont, *Annales Chim. Phys.*, 3d ser., XXXII (1851), 140.

[3] Rickard, *Trans. A.I.M.E.*, XXVI (1896), 978.

[4] Van Hise, *U.S.G.S. Monograph* 47 (1904), 1099.

[5] Spring, *Ber. Deutsch. Chem. Gesell.*, XVI, 324, 1002; XVII, 1218.

[6] Moesta, F. A., *Über das Vorkommen der Chlor-, Brom-, und Jodverbindungen des Silvers in der Natur; ein Beitrag zur Kenntn. d. geol. u. bergbaulichen Verhältnisse von Nord-Chile.* Marburg, 1870.

PREVIOUS WORK—FIELD DATA

Field data bearing on this problem are abundant so far as the paragenesis is concerned but few attempts have been made to discuss the problems in the light of chemical principles. The most suggestive contribution to the literature of the subject is by Weed.[3] He regards the presence of pyrite in silver lodes as prerequisite to the secondary enrichment of silver, and states that, in his experience, notable secondary enrichment has taken place only where there has been pyrite in abundance; where pyrite has not occurred in considerable amount, secondary concentration has not taken place even though all other conditions were favorable. If this relationship is true, then the solution of primary silver sulphides in meteoric waters must depend either (*a*) on the action on the silver minerals of the oxidation products of the pyrite, which may form according to the equations $FeS_2+7O+H_2O=FeSO_4+H_2SO_4$ and $2FeSO_4+H_2SO_4+O=Fe_2(SO_4)_3+H_2O$, or (*b*) on the direct oxidation of the silver minerals, due to the electrolytic action of the silver sulphide-pyrite couple, as recently described by Gottschalk and Buehler,[4] or (*c*) on a combination of these two actions.

In addition to the work of Weed, we have the evidence afforded by analyses of mine waters. While the waters collected from a mine may differ slightly in composition from the ground-waters that seeped through the undisturbed deposit, in that they are probably more dilute on account of the freer circulation of the solutions, and are also more highly oxidized on account of greater access to the atmosphere, yet nevertheless their composition approaches fairly closely that of the original ground-waters. The following tables include most of the complete analyses that have

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[1] Plattner, C. F., *Die Metallurgischen Rostprocesse*. Freiberg, 1856.

[2] Stokes, *Economic Geology*, I (1906), 649.

[3] Weed, *Trans. A.I.M.E.*, XXX, 431.

[4] *Op. cit.*

	1*	2*	3†	4†	5†	6†	7†
SO_4	43.2	161.7	380.38	474.0	209,100.0	173.4	272.3
Cl	7.9	186.4	1.27	19.0	127.6	0.52	13.77
CO_3	110.5	1513.4	115.0	20.5	Undetermined	47.7	241.4
SiO_2	25.9	24.4	30.5	133.4	616.0	37.8	59.9
K	10.6	198.0	8.4	53.4	....	62.26	80.9
Na	36.4	719.4	57.1	132.0	535.0	0.27	6.86
Ca	37.4	146.4	148.1	100.1	1,286.0	72.4	113.7
Mg	12.25	177.7	154.0	5.9	6,590.0	......	......
Al	0.4	1.0	......	1.37	9,670.0	......	......
Mn	0.8	0.6	......	......	885.0	......	......
Fe''	0.7	3.5	......	......	....	......	......
Fe'''				6.33	5,025.0		
Acidity	......	......	......	......	147.5	......	......
Cu	......	......	......	......	....	......	......

	8†	9‡	10‡	11§	12§	13§	14§
SO_4	160.0	7.7	7.8	258.4	26.55	280.1	124.8
Cl	16.82	3.16	3.1	Tr.	Tr.	Tr.	12.4
CO_3	194.7	141.8	146.6	......	.....	......	......
SiO_2	68.9	32.7	41.4	2.1	8.0	8.8	18.0
K	254.1	1.0	1.6	......	.....	......	......
Na	7.84	13.4	13.7	......	.....	......	......
Ca	84.08	33.6	44.35	90.76	72.48	106.2	46.4
Mg	......	5.7	3.35	13.1	14.9	17.1	14.5
Al	......	......	......	1.5	0.4	1.5	......
Mn	......	0.27	1.9	4.7	4.1	1.9	......
Fe''	......	......	......	......	.....	......	6.6
Fe'''	Tr.	......	......	4.7	6.3	4.7	......
Acidity	......	Alkaline	Alkaline	......	.....	......	......
Zn	......	......	......	2.8	47.4	18.88	8.9

	15‖	16‖	17¶	18**	Average
SO_4	60.12	104.4	2039.5	327.2	179.0, excluding 5 and 17
Cl	Tr.	1.6	8.16	35.6	7.7, excluding 2 and 5
CO_3	78.3	92.4	......	87.9	116.0, excluding 2, 5, 11–14, 17
SiO_2	32.25	23.2	43.8	64.8	38.6, excluding 5,
K	2.4	3.5	70.0	3.4	27.0, excluding 2, 5, 8, 11–14
Na	28.5	7.5	106.3	148.8	46.5, excluding 2, 5, 11–14
Ca	17.3	46.2	187.2	68.8	83.2, excluding 5
Mg	1.3	7.3	93.5	6.3	40.0, excluding 5–9
Al	......	......	3.12	......	1.5, excluding 3, 5–10, 14–16, 17
Mn	0.3	3.2	155.6	0.7	2.0, excluding 3–8, 14, 17, 18
Fe''	1.5	0.9	164.8	......	
Fe'''	......	......	......	0.7	
Acidity	Alkaline	Alkaline	......	......	
Zn	......	......	49.66	......	
Cu	......	......	......	77.05	

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* S. F. Emmons, 17th *Ann. Rep. U.S.G.S.*, Part 2, p. 462.

† Reed, *Bull. Dept. Geol. U. of California*, 4, pp. 189 and 192.

‡ Lindgren, 17th *Ann. Rep. U.S.G.S.*, Part 2, p. 121.

§ Beck, *Nature of Ore Deposits*, Weed's translation, II, 377.

‖ W. H. Emmons, unpublished manuscripts.

¶ L. J. W. Jones, *Proc. Colo. Sci. Soc.*, VI (1897), 48.

** R. C. Wells.

been made of the waters of gold and silver mines. For them the writer is indebted to Professor W. H. Emmons who has very kindly placed at his disposal the data which he is about to publish concerning secondary enrichment. The figures given are in parts per million.

1. Geyser silver mine, Custer Co., Colo., 500-foot level.
2. Same, 2,000-foot level.
3. Comstock lode, Savage mine, 600-foot level.
4. Comstock lode, G. and C. shaft, 2,250-foot level.
5. Comstock lode, Comstock mine, vadose water.
6. Comstock lode, Gould and Curry mine, 1,700-foot level.
7. Comstock lode, Hale and Norcross mine.
8. Comstock lode, Gould and Curry mine, 1,800-foot level.
9. Nevada City, Cal., Federal Loan mine, 400-foot level.
10. Nevada City, Cal., Black Prince mine, 400-foot level.

11–14. Rothschonberger Stolln, Freiberg, Germany.

15. Creede, Colo., Bachelor mine, 1,300-foot level.
16. Creede, Colo., Solomon mine, 1,500-foot level.
17. Idaho Springs, Colo., Stanley mine.
18. Tonopah, Nev., Mizpah mine; water from a bore hole 2,316 feet deep.

A study of these data shows clearly that the salts most abundant in mine waters are the sulphates, and further, that there is usually present an excess of acid radicles over basic; i.e., the solutions are acid in most cases. The preceding analyses are all of waters taken at some depth, hence must be assumed to be much more nearly neutral than the waters near the surface, since the tendency of descending waters is to become less acid through reaction with minerals. At Creede, as will be noted, the waters at the 1,500-foot level have actually become alkaline through the solution of carbonate in excess. It is a significant fact that this level is below the zone of secondary enrichment.[1]

The amount of ferric and ferrous salts present in the waters, as shown by the analyses, is surprisingly small. This is probably to be explained by the fact that iron salts are very easily precipitated by carbonates, which are here present in large amount. On the whole, the analyses tend to confirm the hypothesis that the active agents in the secondary processes are acid sulphate waters. They would also suggest that carbonate solutions may be a factor in the processes, but this supposition should be confirmed by analyses of waters from horizons somewhat nearer the surface than those from which the above samples were taken.

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[1] W. H. Emmons, unpublished manuscript.

EXPERIMENTAL WORK

The experimental work described in this paper deals with the following questions:

a) Solvent effect of sulphuric acid and ferric sulphate on argentite and its associated sulphides; both natural and chemically pure artificial minerals being used.

b) The solvent effect exerted on metallic silver by the various reagents that may occur in ground-waters, such as sulphates, chlorides, nascent chlorine, sulphuric and hydrochloric acids.

c) Solvent effect of ferric sulphate solutions on silver chloride.

d) Effect of the presence of ferric sulphate on the solubility of silver sulphate.

e) The equilibrium in dilute solutions between ferric, ferrous, and silver sulphates and native silver.

f) The substitution of silver for antimony or arsenic in the previously formed sulphides of these elements.

g) The reaction of metallic silver with precipitated sulphur.

As these experiments deal with somewhat widely different subjects, each series will be described and discussed separately. All of them were made under conditions approximating those which obtain in ground-waters. The temperatures were uniformly room temperatures, about 22° C. Pressures were atmospheric pressures. Concentrations of solutions were small, usually decinormal; these, although somewhat greater than those that obtain in ground-waters, may be confidently assumed to cause differences only in the speed, and not in the nature, of the reactions which take place.

The paper also includes a discussion, based on the experimental work of Barlow[1] and Schierholz,[2] of the effect of chloride solutions on the solubility of silver chloride, and the precipitation of the silver from such solutions as sulphide.

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[1] Barlow, *Jour. Am. Chem. Soc.*, XXVIII (1906), 1446.

[2] Schierholz, *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften zu Wien*, 101, *2b* (1890), 8.

METHOD OF PROCEDURE

The mineral to be tested was first powdered. In the preliminary experiments natural minerals were used, and only that portion which would pass through a 40-mesh sieve was used. It was thought, however, that the unequal sizing of the mass of mineral so obtained might affect the results materially. Therefore in the later experiments with chemically pure materials, only the fraction that passed an 80-mesh and was held by a 100-mesh sieve was used. Of this material a certain amount, usually 1.0000 gm., was weighed out, washed into a flask, and covered with 200 c.c. of the solution whose action was to be tested. The corked flask was then set away in the dark room at room temperature. After standing for a period of from one to three months, during which time the flask was shaken almost daily, the contents were analyzed. In some cases the analysis was of the liquid contents, after the solid residue had been removed by filtration; in others, where such analysis would prove difficult, it was thought sufficient to determine the materials in solution qualitatively, and the loss of weight of the solid residue. The latter was done by filtering into a weighed Gooch crucible, drying at 120° C., and weighing. This procedure was always adopted when the minerals used were the double sulphides pyrargyrite and polybasite.

Where stibnite was the sulphide acted upon, the procedure differed, in that the solutions themselves were analyzed. This was done because of the ease of the analysis and for the greater accuracy thereby obtainable. In the absence of ferric sulphate the solutions were repeatedly evaporated to dryness in the presence of nitric acid. The resulting precipitate was then heated to a dull-red heat, whereby it was converted into the oxide Sb_2O_4, then cooled, and weighed. Where ferric sulphate was present, hydrogen sulphide was passed in until there was no further precipitate. The solution was then filtered, the filtrate being repeatedly passed through the filter until clear, after which the precipitate was dried and washed with carbon disulphide to remove excess of sulphur. The antimony trisulphide remaining on the filter was redissolved in concentrated hydrochloric acid, the resulting solution mixed with concentrated nitric acid, and cautiously evaporated on a water bath. As fast as the solution became colorless, more nitric acid was added, until further addition caused no change of color. The solution was then evaporated to dryness, the precipitate heated to a red heat, cooled, and weighed. Trial of this method with a weighed amount of pure antimony trisulphide showed it accurate to 1 per cent.

MAKING UP SOLUTIONS

A ferric sulphate solution was made, containing 35 grams of Kalhbaum's C.P. powdered ferric sulphate per liter. This gave a solution nearly F/20 (actually 0.0535 F. An F/1 solution = solution containing 1 formula weight in grams per liter). The sulphuric acid solution used was roughly F/20. That used in the first series of experiments was 0.0635 F; that used in the second series, 0.0502 F. These solutions will hereafter be mentioned simply as "ferric sulphate solution" and "decinormal sulphuric acid," and in the tables will be designated as "F" and "A," for brevity. A proportionality, such as A:F::1:3, indicates the proportions of acid and ferric solutions. The total volume of all solutions, unless otherwise stated, is 200 c.c.

ACTION OF SOLUTIONS ON MINERALS. SERIES 1

As may be seen from the tables, this series of tests included not only the silver minerals, but also those with which it is most closely associated, i.e., the sulphides of arsenic, antimony, and lead. Copper sulphide was not tested, since Vogt[1] had already proved its ready solubility in ferric solutions. The table also shows that both the dilute sulphuric acid and the dilute ferric sulphate solutions exert a powerful solvent action on all the minerals tested except argentite; that in each case the action is much more powerful when ferric sulphate is present; and that, except in the case of galena, an increase in the concentration of the ferric sulphate does not cause a corresponding increase in the solvent action. The absence of results in the case of the lump argentite is rather to be ascribed to the smallness of the surface exposed than to an actual absence of action. This will be shown in the table (Series 2).

[1] Vogt, *Genesis of Ore Deposits* (1896), p. 676, footnote.

SERIES 1

Solution	Mineral	Loss of Weight	Time	Remarks
H_2SO_4......	Pyrargyrite 1.000 gm.	0.0130 gm.	81 days	Solution contained Sb, Ag
Acid: Fer. Sulph. = 3:1 .	Pyrargyrite 1.000 gm.	.0290	81	Solution contained Sb, Ag
A:F::1:1...	Pyrargyrite 1.000 gm.	0.0272	81	Solution contained Sb, Ag
A:F::1:3..	Pyrargyrite 1.000 gm.	0.0268	81	Solution contained Sb, Ag
A..........	Polybasite	.0075	81	Solution contained Sb, Ag
A:F::1:1...	Polybasite	.0212	81	Solution contained Sb, Ag
A..........	Argentite, lump	.0000	83	
A:F::3:1...	Argentite, lump	.0000	83	
A:F::1:1...	Argentite, lump	.0002	83	
A:F::1:3...	Argentite, lump	.0022	83	
Water......	Argentite, lump	.0010	83	
A..........	Orpiment	0.0108	81	Solution contained As
A:F::1:1...	Orpiment	.0780	81	Solution contained As
Water......	Stibnite	....	102	Some sol. lost. Test gave a little Sb and SO_4
A..........	Stibnite	....	102	Solution analyzed, yielded .0185 gm. Sb_2O_4
A:F::1:1...	Stibnite	....	102	Solution analyzed, yielded .0255 gm. Sb_2O_4 solutions of 500 c.c. in each case
A..........	Galena 1.000 gm.	.0714 gm. gain of weight	81	Residues gained in weight due to formation of $PbSO_4$. 75 c.c. of solution used in each case
A:F::2:2...	Galena	.0924 gm. gain	81	
A:F::1:2...	Galena	.1700 gm. gain	81	

The fact that the solubility of the sulphides is so much greater in the presence of ferric sulphate, but is not at all proportional to the concentration of the latter salt, is probably to be explained by the hypothesis that the active agent is really the sulphuric acid, while the ferric sulphate exerts little direct action. The reaction of sulphuric acid on a sulphide may be represented by the equation $Ag_2S+H_2SO_4=Ag_2SO_4+H_2S$. This reaction, like most others, comes to an equilibrium. It must stop as soon as the product of the concentrations of the silver ion and the sulphide ion in the solution becomes equal to the solubility product of the sulphide acted upon (in this case Ag_2S). As the solubility products of most of the insoluble sulphides are very small,[1] the reaction in these cases can proceed but for an almost immeasurably short distance before stopping. But if some substance present remove the hydrogen sulphide as fast as formed, the reaction may proceed till all the ferric sulphate is used up. This is probably the main function of the ferric sulphate, which reacts thus with hydrogen sulphide: $Fe_2(SO_4)_3+H_2S=2FeSO_4+H_2SO_4+S$. If this be the true explanation of the action of the ferric sulphate, then it is to be expected that a small amount of ferric sulphate would cause as powerful a solvent action as a larger amount. The increased action in solutions more concentrated in ferric sulphate, shown especially in the case of the galena, may be ascribed either to a direct oxidizing effect of the sulphate on the sulphide or to the increased speed with which the more concentrated sulphate solution destroys the hydrogen sulphide formed.

If this explanation of the function of the ferric solution be the true one, two questions naturally arise: (*a*) Why is a measurable loss obtained experimentally when pure sulphuric acid acts on the sulphides? and (*b*) Was the reaction really at an end when the measurements taken in the experiments were made? In answer to question (*a*) the writer suggests that the oxygen of the air acts like the ferric sulphate, in removing hydrogen sulphide from solution, thus: $H_2S+O=H_2O+S$; its action is much slower than that of the ferric sulphate, however, so that the action of the acid on the sulphide is less. In answer to question (*b*), we must conclude in the light of the hypothesis given that the action of the acid on the sulphide was not at an end, nor would it end till the ferric salt or the sulphide was used up. This might be tested by a series of experiments similar to the above, and lasting for a year or more; but time did not permit such test.

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[1] Knox, *Trans. Faraday Soc.*, IV (1908), Part I, p. 29. Knox determined the solubility product of Ag_2S as 3.9×10^{-50}; of CuS as 1.2×10^{-42}; of PbS as 2.6×10^{-15}.

ACTION OF SOLUTIONS ON MINERALS. SERIES 2

To make certain that the losses in weight obtained in the last table were not due to the presence of soluble impurities in the natural sulphides, some of the above experiments were repeated with chemically pure substances. For the pyrargyrite used the writer is indebted to Mr. Sayrs A. Garlick, of the department of chemistry, who prepared it according to Sommerlad's method.[1] The other substances were prepared by the writer. The results are given in the following table.

SERIES 2

Solution	Mineral	Loss of Weight	Time	Remarks
Water.........	Argentite	0.0010 gm.	98 days	
A.............	Argentite	.0019	98	
A:F::3:1......	Argentite	.0062	98	
A:F::1:3......	Argentite	.0074	98	
Water.........	Pyrargyrite	.0111	101	
A.............	Pyrargyrite	.0093	101	
A:F::3:1......	Pyrargyrite	.0120	101	
A:F::1:1......	Pyrargyrite	.0125	101	
A:F::1:3......	Pyrargyrite	.0144	101	
Water.........	Stibnite	.0175	84	Weights give weight of Sb_2O_4 obtained from analysis of solutions
A.............	Stibnite	.0205	84	
A:F::3:1......	Stibnite	.0185	84	
A:F::1:3......	Stibnite	.0160	84	
F.............	Silver chloride	......	33	Solutions gave no Ag
F:H_2O::1:1....	Silver chloride	.0000	33	
N/5 H_2SO_4.....	Silver chloride	.0000	33	

It will be seen therefore that the reactions noted in Series 1 and 2 are of the same class. The values obtained in Series 2 are perhaps somewhat smaller than those in Series 1, but this may have been due to the presence of a soluble impurity in the natural minerals; or perhaps the artificial materials may actually dissolve less readily than the natural. The results obtained from Series 1 are, however, fairly well substantiated, and the additional conclusion might be drawn that, in the case of the double compounds of silver with antimony or arsenic, it is the silver which is the less soluble constituent. This result is inferred from observation of pyrargyrite during the reaction; it turned black within a very few days, an effect which could be due only to accumulation of silver sulphide on its surface as antimony was leached out. The writer did not confirm this conclusion by analysis, however.

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[1] H. Sommerlad, *Zeit. anorg. Chemie*, XV (1897), 173.

EFFECT OF NATURAL REAGENTS ON METALLIC SILVER

In the investigation of the effects that the substances in solution in natural waters might have upon metallic silver, the reagents used were sodium chloride solution, hydrochloric acid solution acidified with sulphuric acid, in the presence of manganese dioxide so as to insure the presence of nascent chlorine, sulphuric acid solution, and ferric sulphate solution. The silver used was chemically pure leaf silver, cut into pieces about 2 sq. cm. in area, freed from all tarnish by scraping with a dull knife, and weighed to 0.00001 gm. on an assay balance. These were placed in large test tubes, covered with 75 c.c. of solution in each case, tightly corked, and placed in the dark for 73 days at room temperature (22° C.). At the close of the time mentioned they were taken out, carefully washed and dried, and weighed. In the cases where the silver had been covered with a coating of chloride, this was removed before weighing by washing with ammonia.

Solution	Loss of Weight of Silver
N/10 NaCl	0.00000 gm.
N/10 NaCl:N/10 H_2SO_4::1:1+MnO_2	.01538
N/10 HCl	.04502
N/10 H_2SO_4	.00019
A:F::1:1	.08252

These experiments show clearly the powerful solvent effect exerted by ferric solutions on native silver. It is probably this reagent which leaches the silver from the outer zones of gold nuggets.[1] The conclusion might also be drawn that the formation of native silver would take place to but a limited extent in the gossans of deposits containing much pyrite.

The solvent action of the acids in the above table is ascribed to the presence of air, which sets up an oxidation potential between the silver and the solution, and thus aids the solution of the silver. Acids cannot attack silver directly in the absence of air, since the solution tension of the silver is less than that of the hydrogen which would thereby be given off. This fact may account in part for the stability of native silver precipitated below the zone of oxidation.

ACTION OF FERRIC SULPHATE ON SILVER SULPHATE

During the course of the above experiments, in some cases unusually high concentrations of silver were noted in the solutions. The solubility of silver sulphate in pure water at room temperature, 22° C., determined by measuring the strength of a solution that had been standing with frequent shaking for some months in contact with solid silver sulphate in the dark, was 6.90 gm. per liter or 0.0211 F. Euler[2] gives a figure somewhat higher than this, 7.70 gm. per liter at 17° C. Wright and Thompson[3] give 7.28 per liter at 18° C. The addition of an ionized sulphate, such as ferric sulphate, would be expected to decrease the solubility of the silver sulphate; since in a saturated solution the ion product $[Ag]^2 \times [SO_4]$ must be a constant. This is not the case here, however. Experiments carried out by leaving solid silver sulphate in contact with ferric sulphate solutions of varying strengths for a month or more in the dark show that the concentration of the silver is actually very considerably higher in the ferric solutions than in the aqueous. The following table (p. 16) shows the results obtained.

It will be noted that even in the most dilute of these solutions the solubility of the silver sulphate is increased by about 10 per cent. The results in the higher concentrations, while interesting from a scientific point of view, are of no significance as regards secondary

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[1] J. M. McLaren, *Gold* (1908), p. 22.

[2] Euler, *Zeit. physik. Chem.*, XLIX (1904), 314.

[3] *Phil. Mag.* (5), XVII (1884), 288.

Strength of Ferric Solution	Concentration of Silver in Solution
0.0000 formula wt. per liter	0.0211 formula wt. Ag_2SO_4 per liter
0.0067	.02324
.0134	.02404
.0267	.02404
.0401	.02476
.0535	.02470
.062	.02508
.124	.02657
.248	.03012
.372	.02908
.496	.02864
.620	.03123

enrichment, as the concentration of ferric salt in earth waters probably never exceeds 0.05 F.

The cause of this behavior may be as follows: silver sulphate ionizes primarily into the ions Ag and $AgSO_4$, secondarily into the ions 2Ag and SO_4. The concentration of the silver *ions* is absolutely limited by the equation $\frac{[Ag]^2 \times [SO]_4}{Ag_2So_4}$ = a constant. The addition of a large concentration of sulphate ions, as by the addition of ferric sulphate, must correspondingly decrease the concentration of the silver *ion* present. Since, however, the concentration of the silver in the solution increases, much of the silver must be present in some non-ionized form. The recent work of Harkins[1] would make it seem probable that the silver is present as part of the complex ion $AgSO_4$, the solubility of which would of course not be affected by the presence of the SO_4 ion.

EQUILIBRIUM BETWEEN FERRIC, FERROUS, AND SILVER SULPHATES

The reaction $Fe_2(SO_4)_3 + 2Ag = 2FeSO_4 + Ag_2SO_4$ has already been studied by Stokes,[2] and the fact noted that it is an equilibrium reaction, which proceeds to the right with rising temperature. In ore deposits where secondary enrichment is going on, the ferric sulphate formed in the upper parts of the oxidized zone must be gradually changed to the ferrous state as the solutions descend, by reaction with hydrogen sulphide sulphides and other reducing agents. A descending solution containing ferric, ferrous, and silver sulphates may thus react with the sulphides with which it comes in contact, perhaps taking more silver into solution, until the concentration of the ferrous salt present reaches a definite relation to that of the ferric and silver salts, expressible by the equation

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[1] Harkins, *Jour. Am. Chem. Soc.*, XXXIII (1911), 1836.

[2] Stokes, *loc. cit.*

$$\frac{C_{Fe'''} \times C_{Ag}}{C_{Fe''} \times C_{Ag'}} = K$$

where

$C_{Fe'''}$ . . . . = concentration of ferric ion in solution
$C_{Fe''}$ . . . . = concentration of ferrous ion in solution
$C_{Ag'}$ . . . . = concentration of silver ion in solution
C_{Ag} . . . . = concentration of metallic silver in solution
K = a constant

Since C_{Ag} is extremely small and a constant, we may divide both members of the equation by it, and obtain

$$\frac{C_{Fe'''}}{C_{Fe''} \times C_{Ag'}} = \frac{K}{C_{Ag}} = K_2, \text{ a constant.}$$

It is evident that, given this constant, and an analysis of the earth waters containing the salts mentioned, at various depths, the horizon at which solution would cease and precipitation would begin can be determined. It becomes, therefore, a matter of importance to determine the value of the constant. To accomplish this, a ferrous sulphate solution was made of about F/20 in strength, by dissolving chemically pure ferrous sulphate in N/50 sulphuric acid solution. The ferrous content of this solution was then determined by standard potassium permanganate, the total iron by reduction with test lead and titration with permanganate, and the total sulphate by precipitation as barium sulphate. To 100-c.c. portions of this solution were then added quantities of a saturated silver sulphate solution varying from 10 c.c. to 100 c.c.; the flasks were immediately corked, the whole securely sealed with melted paraffin to prevent access of air, and set away to come to equilibrium. German standard pipettes were used throughout in measuring the solutions. Precipitation of silver, which came down as a cloud of silvery flakes, took place almost at once, and equilibrium was probably reached in a few hours; but owing to delays the solutions remained for 65 days before they were analyzed. They were shaken at intervals during this time. In the analyses, the ferrous salt was first determined by standard permanganate; great care being taken to stop the titration as the first faint tinge of pink appeared. The silver was determined in the same sample by titration with ammonium thiocyanate.[1] The method was found very accurate, duplicates checking to one-tenth of 1 per cent. The ferric salt was determined by difference. In calculating the constant from the results obtained, it was assumed that the salts were all completely ionized in the dilute solutions used. This assumption is scarcely permissible; but the writer was unable to obtain any figures on the ionization of ferric sulphate in solutions of different strengths and for the other salts the difference between complete ionization and their ionization in these solutions is small. Concentrations in the following table are all given in formula weights per liter.

$Fe_2(SO_4)_3$	$FeSO_4$	Ag_2SO_4	K_2
0.00370	0.03972	0.000439	212.1
.00475	.03370	.000703	200.4
.00556	.02876	.000952	203.2
.00626	.02451	.001298	196.7
.00677	.02101	.001708	188.8
.00695	.01849	.002294	163.5
.00718	.01614	.002738	162.5
.00737	.01406	.003226	162.5
.00748	.01231	.003715	163.7
.00749	.01094	.004200	163.0

From the results of the last five analyses the constant would be 163. The higher results of the first five analyses are ascribed to increasing hydrolysis of the ferric salt as its dilution increases. This would make the amount of the ferric *ion* in solution less than the total ferric value. It is the latter which is measured, while only the ionized portion enters into the equilibrium. Therefore, since in the fraction $\frac{C_{Fe}'''}{C_{Fe}'' \times C_{Ag}'}$ the numerator is too large, the value of the fraction must likewise be too large. If this is the true cause of the increase of K_2, an increase of the acidity of the solution by addition of sulphuric acid should bring K_2 back to its true value, by decreasing the hydrolysis of the ferric sulphate. This, however, has not yet been experimentally verified.

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[1] Volhard, *Liebig's Ann. d. Chem.*, CXC, 1.

This constant is given with some hesitation; it should be verified by further experimental work before final acceptance. Moreover, as it stands it expresses a relation merely between the concentrations of the various salts involved, not between the concentrations of their ions; but in the absence of accurate determinations of the extent of ionization of these salts, this is unavoidable.

REACTION OF SILVER CHLORIDE WITH SODIUM CHLORIDE

The question of the secondary enrichment of silver deposits through the agency of chloride solutions has long been discussed. Silver chloride has a solubility in water of 0.0016 gm. per liter at 20° C.[1] It has often been stated that the presence of sodium chloride in the water increases the solubility. The information already at hand in regard to this question is comprised in the following table:

NaCl in Solution	AgCl in Solution	Temperature
gm. per liter	gm. per liter	
34.3	0.0018	20° C.**
46.0	.0025	20° C.
57.5	.0047	20° C.
76.7	.0125	20° C.
115.0	.031	20 °C.
153.0	.090	20° C.
230.0	.313	20° C.
100.0	.025	15° C.†
142.9	.071	15° C.
181.8	.182	15° C.
219.8	.439	15° C.
235.3	.706	15° C.
256.4	1.03	15° C.
263.1	1.27	15° C.

** Barlow, *Jour. Am. Chem. Soc.*, XXVIII (1906), 1446.

† Schierholtz, *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften zu Wien*, 101, 2*b* (1890), 8.

Thus it requires the presence in solution of 34.3 gm. of sodium chloride per liter, or 34,300 parts per million, to raise the solubility of the silver chloride to its value in pure water. In all sodium chloride solution of less strength the solubility of the silver chloride must be less than its solubility in pure water; the solubility curve will consequently be as shown in Fig. 1, which was obtained as follows: silver in chloride solutions exists in two forms, as silver ion and as part of some non-ionized molecule or some complex ion. The concentration of the silver ion in solution is inversely proportional to that of the chloride ion according to the equation $C_{Ag} \times C_{Cl} = k$, a constant. Hence addition of sodium chloride to silver chloride solution will very rapidly reduce the concentration of silver ion to a very small quantity (see Fig. 1). Silver in the non-ionic form may be present as molecular silver chloride, but the amount of this is so small as to be negligible; it may also be present in combination with sodium chloride, forming compounds of composition as yet undetermined, but which may be supposed, from analogy with the corresponding cyanide compounds, to have the formulae $NaAgCl_2$ or Na_2AgCl_3. The silver would then enter into solution as part of the complex negative ion $AgCl_2'$ or $AgCl_3''$, whose solubility would not be affected by the presence of chloride ion. The table shows that the amount of AgCl in solution as complex ion attains 0.0018 gm. per liter only when the amount of sodium chloride present is 34.3 gm. per liter, and that thereafter the concentration of complex ion increases proportionally much faster than does the concentration of the soldium chloride; hence it is probable that in sodium chloride solutions of strength less than 34.3 gm. per liter the concentration of complex ion, and therefore that of silver, will never be more than proportional to the amount of sodium chloride present, but usually less. The curve showing the total silver in solution will consequently be of the form shown in Fig. 1.

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[1] Kohlrausch, *Zeit. phys. Chem.*, L, 356.

From these experiments, therefore, it is concluded that only when the amount of sodium chloride in ground-waters exceeds 34.3 gm. per liter may such waters be solvents superior to those in which chlorides are absent. Such concentrations occur rarely in nature.

An accurate determination of the strength of the sodium chloride solution which contains the minimum amount of silver chloride will be of value as rendering possible the determination of the

Normal or Alkalcic Igneous Rocks

				PLUTONIC	**HYPABYSSAL**		**VOLCANIC**		
					Aschistic	**Felsic Mafic**			
Texture				**Granitic**	Porphyritic with coarse groundmass	Pegmatitic, aplitic, or porphyritic	**Felsitic, or porphyritic with dominant groundmass**	**Glassy**	
ALKALIFELDSPAR	**Soda-lime feldspar present**	**Pyroxene, Amphibole, Mica**	**+Quartz**	**Granite**	Nevadite	Pegmatite Aplite	**Rhyolite**	**Rhyolitic**	**Obsidian**
			−Quartz	**Syenite**	Syenite-porphyry	Syenite-Aplite Minette	**Trachyte**	**Trachytic**	**Pumice**
SODA-LIME FELDSPAR	**Acid plagioclase**	**Amphibole, Mica**	**+Quartz**	**Tonalite**	Tonalite-porphyry	Plagiaplite	Dacite	**Dacitic**	**Pitchstone**
			−Quartz	**Diorite**	Esterellite	Malchite Kersantite	**Andesite**		**Perlite**
	Basic plagioclase	**Pyroxene**	**−Olivine**	**Gabbro**	Gabbro-porphyry	Gabbro-Aplite Beerbachite	**Auganite**	**Andesitic**	**Scoria**
			+Olivine	**Olivine-gabbro**	Olivine-gabbro-porphyry	Garewaite	**Basalt**		**Tachylyte**
NO FELDSPAR	**No feldspathoid**	**Pyroxene,Amphibole, Mica**	**−Olivine**	**Pyroxenite**			**Augitite (in part?)**	**Basaltic**	
			+Olivine	**Peridotite**			**Picrite**		

Alkaline Igneous Rocks

				PLUTONIC	**HYPABYSSAL**		**VOLCANIC**		
					Aschistic	FELSIC Mafic			
Texture				**Granitic**	Porphyritic with coarse groundmass	Pegmatitic, aplitic, or porphyritic	**Felsitic, or porphyritic with dominant groundmass**	Glassy	
ALKALIFELDSPAR	**Soda-lime feldspar absent**	**Soda-pyroxene Soda-amphibole, Mica**	**+Quartz**	**Alkali-granite**	Alkali-granite porphyry	ALKALI-APLITE	**Alkali-rhyolite**	**Pantelleritic**	**Obsidian**
			−Quartz	**Alkali-syenite**	Alkali-syenite porphyry	BOSTONITE Natronminette	**Alkali-trachyte**		**Pumice**
SODA-LIME FELDSPAR	Acid plagioclase With equal alkalifeldspar	**Pyroxene, Amphibole, Mica**	**+Quartz**	**Quartz-monzonite**	Quartz-monzonite-porphyry	QUARTZ-MONZONITE-APLITE	**Quartz-latite**		**Pitchstone**
			−Quartz	**Monzonite**	Monzonite-porphyry	MONZONITE-APLITE	**Latite**	**Latitic**	**Perlite**
	Basic plagioclase **with little orthoclase or lenad**	**Pyroxene, Soda-Amphibole, Mica**	**−Olivine**	**Essexite**		ESSEXITE-APLITE Camptonite	**Trachydolerite**		**Scoria**
			+Olivine	**Olivine-essexite**			**Olivine trachydolerite**	**Doleritic**	**Tachylyte**
NO FELDSPAR	**No feldspathoid**	**Soda-pyroxene, Soda-amphibole, Mica**	**−Olivine**	**Alkali-pyroxenite**			**Augitite**		
			+Olivine	**Alkali-peridotite**			**Limburgite**		

Peralkaline Igneous Rocks

				PLUTONIC	HYPABYSSAL		**VOLCANIC**	
					Aschistic	Felsic Mafic		
Texture				Granitic	Porphyritic with coarse groundmass	Pegmatitic, aplitic, or porphyritic	**Felsitic, or porphyritic with dominant groundmass**	Glassy
ALKALIFELDSPAR	**Feldspathoid present**	Soda-pyroxene **Soda-amphibole, Mica**	+Quartz					Obsidian
			−Quartz	**Nepheline-syenite**	Nepheline-porphyry	Tinguaite	**Phonolite**	Phonolitic Pumice
SODA-LIME FELDSPAR	Acid plagioclase With equal alkalifeldspar and feldspathoid	Pyroxene, Soda-amphibole, Mica	+Quartz					Pitchstone
			−Quartz	**Nepheline-monzonite**	Nepheline-monzonite-porphyry	Allochetite	**Latite-phonolite**	Perlite
	Basic plagioclase **with feldspathoid**		−Olivine	**Theralite**		Fourchite	**Tephrite**	Scoria
			+Olivine	**Olivine-theralite**			**Basanite**	Tephritic Tachylyte
NO FELDSPAR	**No feldspathoid**	Soda-pyroxene, Soda-amphibole, Mica	−Olivine					
			+Olivine					

causes of secondary cerargyrite enrichment in any deposit, because silver solutions containing less sodium chloride than this "minimum solution" will precipitate silver chloride if the concentration of the sodium chloride increases; while, on the contrary, silver solu-

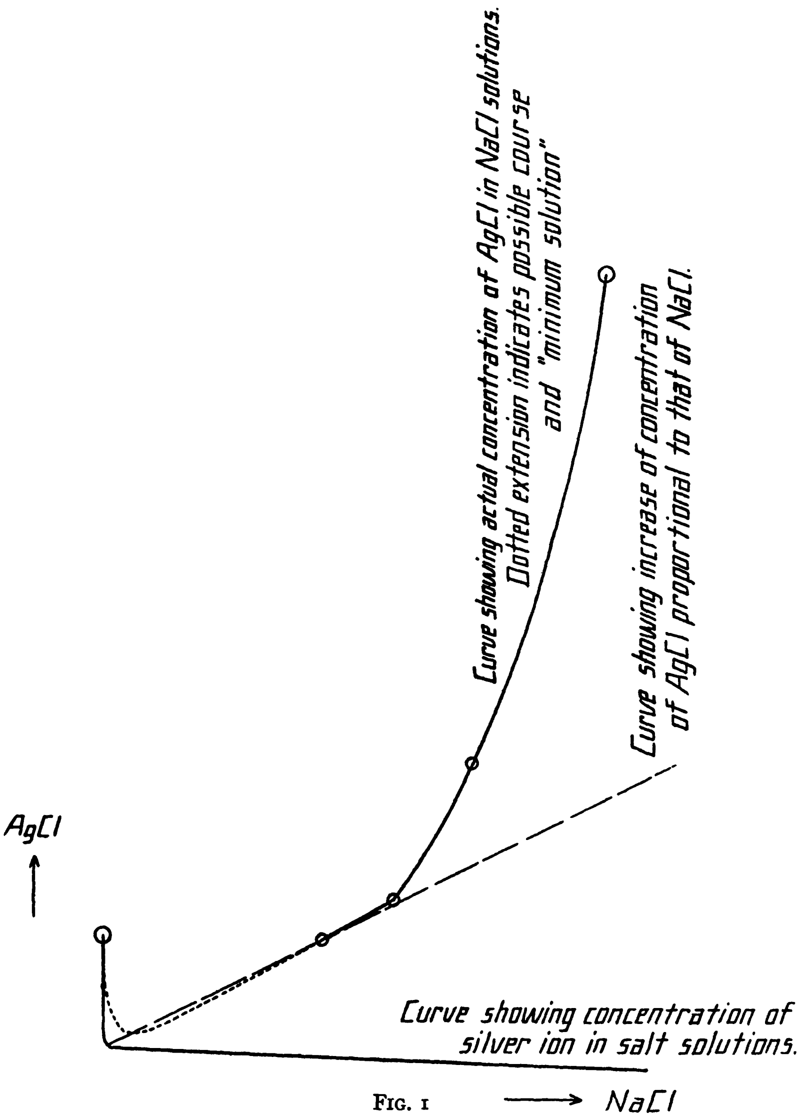

Fig. 1

tions in which more sodium chloride is present than in the "minimum solution" will precipitate silver chloride *on dilution.*

Can the addition of sodium chloride to silver chloride solutions ever so reduce the amount of silver present that the precipitation of silver as sulphide becomes impossible?

This relation is determinable mathematically. The solubility of silver chloride in water at 20° C. is 0.0016 gm., or 1.1×10^{-5} mols per liter. Assuming complete dissociation, as is permissible at such dilutions for a salt of a strong acid and a strong base, we should have present in solution 1.1×10^{-5} mols of Ag ion, and the same number of mols of Cl ion. The solubility product for the salt is therefore $(1.1 \times 10^{-5})^2 = 1.24 \times 10^{-10}$.

The concentration of silver sulphide aqueous solution is 2.2×10^{-17} mols per liter,[1] and at such extreme dilution the salt may be assumed to be completely ionized. The amount of Ag ion present in a saturated solution is therefore 4.4×10^{-17} mols per liter, and the amount of sulphur ion, one-half of this.

The addition of sodium chloride to silver chloride solution, as before shown, decreases the amount of silver ion present in solution. To prevent the precipitation of the silver as sulphide, the amount of silver ion would have to be decreased till the product of the silver ion and the sulphur ion present in solution was equal to the solubility product for silver sulphide, i.e., 3.9×10^{-50}. If we assume the concentration of sulphur ion never greater than the amount given above, 2.2×10^{-17}, then the concentration of the silver ion must decrease to 4.4×10^{-17} if precipitation is not to occur. Substituting this value into the equation $C_{Ag} \times C_{Cl} = 1.24 \times 10^{-10}$, we obtain 2.8×10^6 as the value of the Cl ion. Disregarding the infinitesimal amount of Cl ion in combination with Ag ion, we should therefore require to have present 2.8 million mols, or about 165 million grams, of ionized sodium chloride per liter, to prevent the formation of silver sulphide under the given conditions. With higher concentrations of sulphur ion, even more sodium chloride would be required to prevent the formation of silver sulphide. As such concentrations of sodium chloride are impossible, it is evident that the amount of this salt in meteoric waters can never rise so high as to bar the precipitation of silver as sulphide from solutions in which it is carried as chloride.

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[1] Knox, *loc. cit.*

MECHANISM OF THE SOLUTION OF SILVER MINERALS IN METEORIC WATERS

The work of Gottschalk and Buehler, coupled with that of the writer, renders possible a statement of the method by which the silver sulphides are taken into solution in the ground-water. The potentials of the minerals studied by Gottschalk and Buehler, measured against that of copper, include marcasite, +0.37 volt; argentite, +0.27 volt; pyrite, +0.18 volt. If we assume then an ore-body of argentite and pyrite, the pyrite, whose potential is lower than that of the argentite, will be oxidized, while the argentite is protected from *direct* oxidation. The silver can then be taken into solution only by the secondary action of the oxidation products of the pyrite, ferric sulphate, and sulphuric acid. But if the iron sulphide of the deposit be marcasite—a rare case—then we might expect a *direct* oxidation of the silver sulphide to sulphate by the electrolytic action set up since marcasite possesses a higher potential than argentite.

Moreover, the iron sulphides are *the only sulphides* which can effect the solution of the argentite. The potential of argentite is higher than that of the sulphide of any other metal except iron, hence it can undergo *direct* oxidation only in the presence of iron sulphide; and since no sulphides but those of iron produce by oxidation the solvents ferric sulphate and sulphuric acid, argentite can undergo *indirect* oxidation likewise only in the presence of iron sulphide. Therefore Weed's deduction, that the secondary enrichment of silver is dependent on the presence of pyrite in the lodes, appears to be confirmed.

FORMATION OF SILVER SULPHIDE

The formation of the complex silver minerals by simultaneous precipitation of the component sulphides was not attempted, on account of lack of facilities for handling large volumes of dilute solutions. It was thought, however, that these might be formed by substitution of silver for arsenic or antimony in the pre-existing sulphides of these elements. To test this theory, well-crystallized specimens of realgar, orpiment, and stibnite were powdered, the stibnite to pass an 80-mesh, the others a 40-mesh screen. The stibnite was covered with a saturated (about N/30) silver sulphate solution, the realgar and orpiment with N/40 silver nitrate solutions, after which the mixtures were put away in the dark. The stibnite was analyzed after 36 days, the realgar and orpiment after 68 days, the analyses being conducted by passing a current of dry chlorine over the material heated to a low red heat. The silver remained in the tube as silver chloride, together with earthy impurities; the other substances volatilized as chlorides. After weighing, the silver chloride was dissolved with warm ammonia, and the weight of the impurities determined. Results were:

Stibnite contained 1.3 per cent Ag
Realgar contained 1.9 per cent Ag
Orpiment contained 9.8 per cent Ag

Since pyrargyrite contains 60 per cent and proustite 65 per cent of silver, the amounts of silver entering into the sulphides in these experiments were far below those necessary to give a true silver mineral. Moreover, the reaction in the case of the orpiment was visibly instantaneous, the powder changing from brilliant yellow to black at once. As the solutions used contained much more silver than ground-waters commonly do, it would appear improbable that true silver minerals are formed in this way.

The formation of argentite can easily be explained by the action of hydrogen sulphide or a metallic sulphide on silver-bearing solutions. As has been shown by R. C. Wells,[1] the action of dilute sulphuric acid on pyrrhotite, galena, sphalerite, and other natural sulphides produces hydrogen sulphide. This might be supposed to react with the silver solution and yield silver sulphide, and, as already mentioned, would do so in the case of chloride solutions carrying silver. But in the case of sulphate solutions a complication is introduced. Hydrogen sulphide would probably precipitate the silver as sulphide here also, but it tends in addition to attack the ferric sulphate present in the solutions, and to reduce it to the ferrous form with separation of sulphur. The formation of ferrous lt would precipitate silver from solution as metal, so that a mix- re of sulphur and metallic silver might result. Sulphur in the dinary form will not react with silver, except under very high essures,[1] which cannot be assumed under the conditions existing. owever, as has been recently shown,[2] precipitated sulphur is ot crystalline, but amorphous, and might therefore be expected to ossess a greater chemical activity than crystalline sulphur. To st this, an acid solution of ferric sulphate was partially reduced ferrous salt by passing in hydrogen sulphide, after which it was lowed to stand for a few minutes in order that all the hydrogen lphide in solution might be used up. Some silver previously recipitated by reaction of ferrous sulphate with silver sulphate as then added. Reaction did not occur at once, but at the end of venty-four hours all of the silver had been altered from silvery hite flakes to black silver sulphide. To make certain that the lack mass did not consist of marcasite, as might be suspected from e work of Allen,[3] some sulphur was precipitated by treating odium thiosulphate with sulphuric acid, filtered, washed, and dded to some washed silver prepared as before. The results were e same, hence the end product of the reaction of hydrogen sulhide with silver solutions is silver sulphide, whether it is the first roduct of precipitation or not.

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[1] R. C. Wells, unpublished manuscript.

The conclusion may also be drawn from this reaction, that if any deposit native silver were the first product precipitated, nd at some subsequent time sulphur were also formed there, then he sulphur and silver would combine to form argentite, the comleteness of the alteration depending on the amount of sulphur. uch a hypothesis might possibly account for the mixtures of econdary argentite and native silver found at depths in some eposits, notably at Creede, Colo.

SUMMARY

Secondary sulphide enrichment of a primary silver deposit is rought about by reactions of silver or its sulphides with the ulphides of iron and their products of oxidation.

[1] Spring, *loc. cit.*

[2] Brownlee, *Jour. Am. Chem. Soc.*, XXIX (1907), 1032.

[3] Allen, *loc. cit.*

When the iron sulphide present is pyrite, the silver sulphide is converted into sulphate wholly by the sulphuric acid and the ferric sulphate produced by the oxidation of the pyrite, according to the equation on p. 5.

When marcasite is present, as it rarely is in quantity, silver sulphide may be oxidized in part directly to silver sulphate by electrolytic action, and in part may be converted into sulphate by the action of the oxidation products of the marcasite.

Sulphuric acid and ferric sulphate exert a powerful solvent action both on silver sulphide and on its companion sulphides, such as galena, chalcocite, orpiment, and stibnite. Of these, silver sulphide is the least affected. In all cases the action is much more powerful when ferric sulphate is present than when sulphuric acid acts alone.

Except in the case of galena, the solvent action does not seem to be proportional to the concentration of the ferric sulphate present. This suggests that the sulphuric acid is really the active agent, and that the ferric sulphate acts principally as an agent for the removal from solution of hydrogen sulphide formed during the reaction.

A mixture of sulphuric acid and ferric sulphate has a powerful solvent action on metallic silver, hence, in an ore-body containing much pyrite, little native silver may be expected in the gossan; and conversely, if much native silver be found in the gossan, the ore-body cannot have contained much pyrite, and little secondary enrichment should be expected.

The presence of ferric sulphate in the ground-waters increases the solubility of silver sulphate in them. This is probably due to the formation of a complex ion $AgSO_4$ by the silver, when ferric sulphate is present in solution.

Equilibrium in silver-bearing solutions between ferric, ferrous, and silver sulphates is such that the reduction of ferric solutions to the ferrous condition by any means will rapidly precipitate the silver in the metallic form. Precipitation of silver will not cease till all the ferric salt is reduced to the ferrous state. Hence the vertical extent of the zone of precipitation and its proximity to the surface will depend on the rapidity with which this reduction goes on. If reduction be slow, native silver may thus be formed even at considerable depths. Native silver so precipitated will be comparatively stable in the presence of earth waters. Acids will not attack it in the absence of oxygen, since the solution pressure of hydrogen is greater than that of silver. Ferric sulphate cannot attack it so long as the ground-waters contain enough silver sulphate to preserve equilibrium between the ferric and ferrous salts. Precipitated sulphur may convert it into sulphide.

The presence of sodium chloride in ground-water does not increase the solubility of silver chloride therein, unless the amount of sodium chloride rises above 34.3 gm. per liter; on the contrary, it decreases the solubility. The solubility-curve of silver chloride in sodium chloride solutions is shown in Fig. 1. Terming the sodium chloride solution which contains the least amount of silver chloride the "minimum solution," then solutions which contain less sodium chloride than this minimum solution will precipitate silver chloride on taking up more sodium chloride; solutions with more sodium chloride than the minimum solution will precipitate silver chloride on dilution.

Silver chloride solutions containing sodium chloride in any concentration may form secondary silver sulphide wherever they encounter hydrogen sulphide or any other substance that yields sulphur ion even in minute quantity.

Cerargyrite appears to be stable in presence of sulphuric acid and ferric sulphate.

The action of dilute silver solutions on realgar, orpiment, and stibnite results in the substitution into these minerals of some silver; but the amounts so substituted were found to be so small that it appears doubtful whether the complex sulpho-salts of silver can be formed in this way.

Precipitated sulphur combines with precipitated silver at ordinary temperature and pressure to form silver sulphide. Silver sulphide is also formed by the direct reaction of hydrogen sulphide with silver-bearing solutions.

CONCLUSION

The accuracy of the application of laboratory investigations to geologic problems must be verified by field observations; otherwise, however correct the experimental work, it cannot be claimed to solve the problem attacked. The data at hand dealing with the secondary enrichment of silver are scarcely complete enough to make such verification of this work at the present time. The full solution of the problem would require (*a*) approximately accurate estimates of the proportions in which pyrite, primary silver sulphide, and secondary silver sulphides are present, in a large number of deposits; (*b*) more analyses of mine waters, and especially of waters from the same mine at different depths; (*c*) further observations on the changes in chemical and mineralogical composition of lodes with depth; (*d*) accurate analyses of the thin veinlets of secondary material that cut primary sulphide ores; (*e*) in cerargyrite deposits, analyses of the waters at top and bottom of the cerargyrite zone. Such data would at once render it possible to determine whether or not the processes of the secondary enrichment were subject to factors other than those mentioned in this paper.

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